

PATENT SPECIFICATION

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NO DRAWINGS.

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COMPLETE SPECIFICATION.

Cellulose Derivatives.

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, of 343 State Street, Rochester, New York 14650, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the treatment of water-soluble esters of cellulose and more particularly to a neutralization and stabilization treatment for freshly prepared monovalent metal cellulose acylate sulphates.

A variety of methods have been described in the prior art for preparing water-soluble esters of cellulose and more particularly water-soluble monovalent metal cellulose acylate sulphates (i.e., esters of cellulose containing more than 6 percent by weight of sulphur). These include the methods of U.S. patents No. 1,866,532; 2,582,009; 2,622,079; 3,075,962; 3,075,963 and 3,075,964. Although the reagents and conditions described in the preparations vary considerably, there is one step of the preparation which remains constant in all of these disclosures. This is the step which calls for washing the freshly prepared product with large amounts of an organic solvent, such as isopropanol or acetone, in order to remove substantially all traces of residual unreacted acids which might cause degradation of the product.

This washing step is often one of the most hazardous and costly of the entire manufacturing operation due to the inflammable and explosive nature of the washing solvents and the extensive equipment and careful handling procedures which must consequently be used.

According to the present invention there is provided a method of neutralizing the residual acidity in water soluble cellulose ester material comprising treating the material in an atmosphere containing at least 25 volume per cent of a gaseous amine or mixture of amines until at least half the residual acidity is neutralized. Ammonia is to be considered as coming within the scope of the term "amine".

The present invention provides a treatment for freshly and heterogeneously (i.e., without dissolution of the cellulose ester) prepared water-soluble cellulose esters and in particular monovalent metal cellulose acylate sulphates, which treatment comprises exposing the freshly prepared, somewhat acidic, cellulosic material to an atmosphere comprising at least 25 volume per cent of a gaseous amine (or mixture of gaseous amines) for a period of time sufficient to neutralize at least 50% of the residual acids which are present within the fibrous product mass.

According to a preferred embodiment, the invention provides for drying a monovalent metal cellulose acylate sulphate prepared according to any conventional heterogeneous reaction technique, preferably in a vacuum, to effect preliminary removal of harmful residual acids and subsequently causing the drying chamber to return to atmospheric pressure by admitting a gaseous amine such as ammonia, methylamine or ethylamine into the chamber which can, but need not, be heated until at least 50 percent and preferably substantially all of the residual acidity has been neutralized.

Although the optimum cellulosic product is one from which substantially all of the residual acidity has been eliminated and, hence, one which possesses a very high degree

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of stability, some improvement in the stability of the product can be obtained if at least half of the acidic materials are neutralized during the practice of this invention. Thus, although it is preferred to treat the cellulosic according to the process of this invention for a period of time sufficient to ensure neutralization of substantially all of the residual acidity, the product may be removed from the treatment prior to the time when this stage is reached and a useful product having only a portion of its residual acidity eliminated via the present process obtained. Generally, however, it is preferred that practically all of such residual acidity be eliminated in the optimum practice of this invention.

One of the preferred classes of materials for treatment in accordance with the present processes consists of the monovalent metal cellulose acetate sulphates which are generally prepared commercially by treating fibrous cellulose as a slurry with acetyl-sulphuric acid (partially as the sodium salt) in an acetic acid-acetic anhydride mixture. At the completion of the reaction, the fibrous product is separated from the sulphating-acetylating bath and slurried in a solution consisting of a neutralizing agent (described in detail below), a stabilizing agent (also described below), a small amount of water and acetic acid. The fibrous product is then separated by filtration and the product dried in a vacuum to remove as much acetic acid as possible. Not all acetic acid will be removed in this fashion, but a small amount of from 1 to 5 percent (based on the product) whose quantity can be determined by titration with any conventional base such as sodium hydroxide will remain. It is at this point that the treatment according to the present invention is applied. The cellulosic product can be treated with a gaseous amine by, for example, permitting the amine to leak into the vacuum drying chamber until atmospheric pressure is attained, thus providing an amine atmosphere of substantially 90-100 percent by volume when the vacuum chamber is essentially evacuated prior to admission of the amine. During the time the amine is leaking into the vacuum chamber, the product is being rendered heat stable, as the amine neutralizes the small amounts of residual (in this instance acetic) acid. The product can then be heated, if desired, to drive off any excess amine which may remain in the fibrous product.

Alternatively, treatment of the cellulosic product with the amine can be carried out in a number of ways. For example, the cellulosic material can be removed from the drying chamber and the gaseous amine passed therethrough at the required concentration in either another chamber which is

at atmospheric pressure, or in an open apparatus fitted with the proper equipment such as an exhaust fan to prevent dispersion of the gas into the air and to provide a means for recovering the unreacted amine for recirculation. If desired, the cellulosic material may be dampened with either water or an organic solvent such as acetone prior to treatment with the amine, as this may in some instances by diluting or dissolving the materials such as the residual acids and salts which import the residual acidity to the cellulosic hasten the neutralization reaction with the amine. If water is used as the dampening agent, however, care should be taken to use no more than 10% by weight thereof due to solubility of the product being treated in water.

Furthermore, it is not essential that the cellulosic material be dried (as described above) prior to treatment with the amine according to the processes of this invention. However, if the cellulosic product is not dried, prior to treatment, a substantially larger amount of the amine will be needed to neutralize the larger amounts of residual acid material which will be present due to a lack of a preliminary removal by drying.

If the cellulose ester is dried by heating in air, the amine atmosphere can be produced by either passing the amine through the fibrous product mass or placing the product in a closed container and pumping the gaseous amine therein. In any case, a sufficient amount of the amine must be brought into contact with the mass to ensure that at least 50% of the residual acid is neutralized to provide the type of a useable product generally desired. As a practical matter, the concentration of the gaseous amine around the cellulosic fibres must be such as to provide an atmosphere of at least 25% by volume of the amine in order to provide the necessary minimal desired effects described above.

The concentration of the amine in the vacuum chamber, or in the atmosphere which contacts the cellulose ester if such a chamber is not used, may range broadly depending upon the amount of time which is available for neutralization of the residual acid as well as the amount thereof which is present in the fibrous product and the percentage of the acid which it is sought to remove. As stated above, the concentration of the amine should be at least 25 volume percent and, preferably, the concentration thereof within and about the product should approach 100 volume percent to ensure rapid and complete neutralization of the residual acidity to obtain the preferred substantially acid-free product.

The cellulose ester and the preferred monovalent metal cellulose acylate sulphates may be prepared according to any of the

heterogeneous reaction methods set forth in the above-mentioned patents or, for that matter, almost any of the conventional heterogeneous prior art procedures. Once the desired salt is obtained from the heterogeneous reaction, the fibres are separated from the liquid phase of the reaction mixture and the same dried, preferably by heating to 66°C. in a vacuum or simply leaving them at room temperature (about 21°C.) in the vacuum, in order to remove as much of the residual acid reagent as possible. Although the heating and the application of the vacuum are not strictly necessary, they hasten evaporation and removal of the acid and, hence, are preferred as a preliminary preparatory step.

The actual amount of time required to neutralize a significant amount of free acid in such cellulosic materials is not critical and can, in fact, vary considerably depending upon such factors as the concentration of amine in the atmosphere with which the cellulosic product is contacted, the temperature during the contacting period, the physical orientation of the cellulosic material (i.e., whether it is "fluffy" or very tightly packed), and even the particular amine that is utilized. However, as a general rule, the period of time during which the gaseous amine is held in physical contact with the acidic cellulosic material is at least 1 second. Contact periods of from 5 minutes to 10 hours will generally be adequate to treat any of the celluloses intended for treatment in accordance with the processes of this invention. In one of the preferred embodiments of the present invention where, for example, a mixture of air and ammonia (about 90—100 volume percent cellulose acetate sulphate, optimum contact ing a bed or layer of dried, somewhat acidic cellulose acetate sulphate, optimum contact time is within the range of from 2 to 5 hours (the temperature of the gas and cellulosic material being about 49°C.). This range is typical of the preferred practice of the present processes.

The monovalent metal cellulose acylate sulphates which are the preferred subjects of this treatment include the salts of lithium, potassium and, according to the preferred embodiment set forth in the examples below, sodium. The acylate portion of the salt may be the acetate, propionate, butyrate or mixtures thereof, whose composition depends upon the method of preparation and the reagents utilized.

Any primary, secondary or tertiary amine having a boiling point below 121°C. can be used in the process of this invention, although those boiling 66°C. should preferably be used under vacuum conditions such as those described below.

Some of the particular amines which are

suitable for use in the present invention include ammonia, alkyl amines, cycloalkyl amines and aryl amines. Such amines include:

TABLE 1	
Ethylamine	70
Methylamine	
Isopropylamine	
Tert-butylamine	
n-propylamine	75
Isobutylamine	
n-butylamine	
Ethylenamine	
Ethylmethylamine	
Dimethylamine	80
Diethylamine	
Methylisopropylamine	
Sec-butylamine	
Trimethylamine	
Ethylpropylamine	85
Di-isopropylamine	
Cyclopropylamine	
Cyclobutylamine	
Pyrrolidine	
n-methylpyrrolidine	90
2,4-dimethylpyrrolidine	
piperidine	

All of the above either boil below room temperature or if they boil above room temperature, may also be used in the treatment of this invention by heating them to their boiling point prior to admitting them to a vacuum treating chamber or bed, the latter chamber or bed being maintained at or above the boiling point of the amine but below the recommended 49—66°C. drying temperature for the salt. Alternatively, the amine can be allowed to boil into a treating chamber which can, but need not, be at reduced pressure. Whatever the amine used, it should have a boiling point such that conversion into a gaseous form does not require heating of the cellulose ester to a temperature above the 49—66°C. range suggested as an optimum drying temperature range. All of the above-mentioned amines boil below the recommended 66°C. maximum drying temperature at atmospheric pressure, or will boil at temperatures within that range under the vacuum conditions which can prevail within the confines of the preferred vacuum drying chamber which is maintained at a maximum pressure of 100 mm/mercury. It should be clear that the higher boiling amines can be used when the vacuum drying and treating method are used, as under such reduced pressure even amines with normal boiling points substantially above the recommended drying temperature range (below 121°C.) will boil within the suggested range. Further preferred for optimum results and treatment simplification are those compounds such as

ammonia, ethylamine and methylamine which boil below room temperature and, hence, do not require heating of or application of a vacuum to the cellulosic material to obtain neutralization according to the processes of the present invention.

As stated above, the preferred subjects for treatment in accordance with the processes of this invention are the monovalent metal cellulose acetate sulphates which can be prepared by treating fibrous cellulose as a slurry with acetylsulphuric acid (partially as the sodium salt) in an acetic acid-acetic anhydride mixture. At the completion of the reaction, which requires about 2 hours, the fibrous product is separated from the sulphating-acetyllating bath by filtration and slurried in a solution consisting of a neutralizing agent such as sodium acetate, potassium acetate, sodium hydroxide, potassium hydroxide, sodium carbonate or some other alkali base or basic salt, a stabilizing agent such as urea, a small amount of water and acetic acid. The neutralizing agent reacts to neutralize any free sulphuric acid which may still be present after the sulphonation reaction, while the stabilizing agent provides a ready source of base ammonia to neutralize any degrading acid which may be formed during storage of the cellulosic.

According to the preferred embodiment, the fibrous alkali cellulose acetate sulphate is then separated by filtration, heated to from 49°C. to 66°C. in a vacuum of from 10 to 100 mm/Hg for from 15 to 120 minutes in order to accomplish preliminary removal of residual acetic acid which is present in the fibrous product as described above.

As a matter of fact, insofar as the successful practice of the present invention is concerned, the particular manipulative procedures (including the concentration and types of the various reactants) used in producing the cellulosic material are not important so long as water-soluble cellulosic materials such as those described herein are produced thereby.

At the end of this time, the heat is removed from the drying chamber and ammonia can be admitted until atmospheric pressure is reached. In this manner a substantially 100 percent amine atmosphere is produced in the vicinity of the fibrous mass. Exposure of the product to this atmosphere for maximum stabilization should range from 5 minutes to 10 hours depending upon the physical form of the product (i.e., "fluffy" or closely packed) and the other variables described above. The product is then removed from the drying chamber.

The excess ammonia which may be present in the fibrous product at this point is easily removed by heating the product to

49°C. for from 5 minutes to up to several hours.

The present processes apparently do not interfere with the function of other materials that are sometimes added to the various cellulosic materials which can be treated in the manner disclosed herein. For example, small amounts of urea can be used in accordance with conventional stabilizing techniques prior or subsequent to treatment according to the method disclosed herein without detracting from the excellent result that can be obtained by practising this invention.

The following examples will serve to illustrate the invention:

EXAMPLE 1

An acetylation grade pulp is water activated and de-watered with acetic acid. Fifty parts of this pulp (containing 46.7 parts of acetic acid) are added to 1,700 parts of acetic acid and the slurry cooled to 17°C.

The sulphating mixture is prepared by adding 51.6 parts of 95% sulphuric acid to a slurry of 71 parts of sodium sulphate in 625 and 129 parts of acetic anhydride and acetic acid respectively. This solution is cooled, 12.3 parts of 95% sulphuric acid added and the final mixture cooled to 0°C.

The sulphating mixture is added to the slowly stirred slurry of pulp in acetic acid and allowed to react for 2 hours (no external cooling required). The mixture comes to room temperature by the end of the reaction. The fibrous product is collected in a suction funnel which gives a filter cake containing 3 parts liquid. The cake is then slurried in a solution containing 25 parts sodium acetate, 20 parts urea, 125 parts water in 2,375 parts acetic acid. After standing in the wash solution for 18 hours, the product is again collected on a suction funnel and finally dried at 60°C. under a 20 mm/Hg vacuum. After vacuum drying, ammonia gas is allowed to leak into the drying chamber until atmospheric pressure is achieved. The product is then removed from the vacuum chamber and subsequently heated in a 49°C. oven for 5 hours to discharge any excess ammonia in the product.

The product is stable to 160°C. for 24 hours and completely water-soluble.

Analyses for the sulphate ester are:

% Total Sulphur	11.7	
% Free Sulphur (Na_2SO_4)	2.6	
% Acetyl	16.4	120
% Ash	30.5	
% Nitrogen	1.6	

EXAMPLE 2

In a 12,000 ml. flask was placed 193.4

grams of pulp (wet with acetic acid, 100 grams when dry) and 3,400 grams of acetic acid. 24.6 grams sulphuric acid (95%) in 200 grams acetic acid were then added to the above mixture and agitated at 25°C. for 1 hour.

The purpose of the sulphuric acid addition is to degrade the pulp in order to obtain a final product which has a lower viscosity.

The following sulphation mixture is added and reacted at 25°C. for 2 hours:

Sulphation Mixture

	Sodium sulphate	142 grams
	Acetic anhydride	1250 grams
15	Acetic acid	258 grams
	Sulphuric acid	103.2 grams

The liquid is removed with suction and the damp product is then kept in the following solution for several hours:

20	Acetic acid	3800 grams
	Water	200 grams
	Sodium acetate	50 grams
	Urea	40 grams

The liquid is suctioned off and the product dried over-night at 60—70°C. under vacuum. It is then dried 2 days at 50°C. in a recirculating air oven to eliminate residual acetic acid.

The product is then placed in an essentially 100% ammonia atmosphere for several hours.

The excess ammonia is eliminated by placing the product in a 50°C. recirculating oven overnight.

The product is stable for 23 hours at 160°C.

	% Acetyl	= 13.9
	% Ash	= 28.4
	% Nitrogen	= 2.4
40	% Total Sulphur	= 11.2
	% Free Sulphur	= 2.0

EXAMPLE 3

In a 12,000 ml. flask was placed 193.4 grams of pulp with acetic acid (100 grams dry) and 3,400 grams of acetic acid.

The following sulphation mixture was cooled to 0°C. and added with agitation:

	Sodium sulphate	142 grams
	Acetic anhydride	1250 grams
50	Acetic acid	258 grams
	Sulphuric acid (95%)	127.8 grams

The heterogeneous mixture was allowed to react at 25°C. for 2 hours and the liquid removed with suction.

The damp product is then placed in the following solution for 5 hours:

Acetic acid	3800 grams	
Water	200 grams	
Sodium acetate	50 grams	
Urea	40 grams	60

The liquid is suctioned off and the product dried overnight at 60—70°C. under vacuum. It is then dried for 48 hours in air at 50°C. to eliminate residual acetic acid. The product is then placed in an essentially 100% ammonia atmosphere for several hours.

The ammonia is eliminated by placing the product in 50°C. air for 16 hours.

Product is stable at 160°C. for 20 hours.

% Ash	= 31.1
% Free Sulphur	= 3.0
% Acetyl	= 16.9
% Total Sulphur	= 11.5

WHAT WE CLAIM IS:

1. A method of neutralizing the residual acidity in water soluble cellulose ester material comprising treating the material in an atmosphere containing at least 25 volume percent of a gaseous amine (as defined herein) or mixture of amines until at least half the residual acidity is neutralized.

2. The method as claimed in Claim 1 wherein the amine has a boiling point below 121°C.

3. The method as claimed in Claim 1 or Claim 2 wherein the material is treated at a temperature from 21°C. to 66°C. for at least one second.

4. The method as claimed in any of the preceding claims wherein the gaseous amine is ammonia or an alkyl, aryl or cycloalkyl amine or mixture thereof.

5. The method as claimed in Claim 4 wherein the gaseous amine is one of those set out in Table 1 herein.

6. The method as claimed in any of the previous claims wherein the gaseous amine or mixtures of amines is admitted into an evacuated chamber maintained at a maximum pressure of 100mm of mercury and containing the cellulose ester material until the pressure reaches atmospheric and heating the material for a period for 5 minutes to 10 hours.

7. The method as claimed in Claim 6 wherein the cellulose ester material is a monovalent metal cellulose acylate sulphate which has been dried in the evacuated chamber at a temperature from 21°C. to 66°C. before the gaseous amine or mixture of amines is admitted.

8. The method as claimed in any of the preceding claims wherein the treated material is heated after treatment to remove any residual amine.

9. Methods of neutralizing the residual

acidity in water-soluble cellulose ester materials as claimed in Claim 1 and substantially as herein described. materials whenever treated by the method of any of the the claims 1 to 9. 5

10. Water-soluble cellulose ester ma-

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